GREAT BRITAIN

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COMPLETE SPECIFICATION

Process for Producing Colour Films by Subtractive Synthesis and its Application to Sound Films

I, MAURICE DEGUIGNES, of French Nationality, of 38, avenue Niel, Paris (17e), France, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

To obtain a positive coloured image by subtractive synthesis, one known method is to superimposed correctly three partial positive images, called mono-chromatic images, corresponding respectively to the colours purple, blue-green and yellow and obtained from three negatives which have been selected respectively for the green, orange and violet colours.

This invention has for its object a process for producing colour film by subtractive synthesis which is more economic than processes known up to the present.

The invention consists in a process for producing colour films by subtractive synthesis, comprising producing on the opposite sides a double-sided film positive silver images by exposing through negatives selected for the green and orange respectively, developing and fixing, treating said silver images with chlorine and then with thioindoxyl and indoxyl respectively so as to produce respectively positive purple and blue-green indigoid dye images together with silver images, whereafter the silver image is removed and a positive image of the yellow colour is superimposed on one of said indigoid images by sensitising with a mixture of an alkali diazo sulphonate with a coupling agent such as 1 phenyl 3 methyl 5 pyrazolone which gives the yellow image by exposure to light through the negative selected for the violet.

The invention also includes the application of the above defined process to the production of coloured films having a sound track in which the sound band is printed after the simultaneous printing of the positive mono-chromatic purple and blue-green images.

[Price 2/-]

A manner of putting the process according to this invention into practice and different modifications of the same will now be described.

After printing simultaneously, in register, the positive mono-chromatic latent images of the purple and blue-green colours, each on one side of a double-sided film provided in known manner with an intermediate red or yellow separation layer which is eliminated during the subsequent treatment of the film, the sound band is printed by means of a suitable machine, preferably on the side of the film which bears the blue-green image.

These three latent images are developed by means of a positive developer of the usual type, so as to obtain images in black and white. This development and the subsequent fixing are best effected on the machines which are usually employed in the cinematographic industry and which are adapted to effect in a single operation all photographic treatments, including the drying of the film.

These operations do not need to be described in more detail since they are as a whole well known in the cinematographic industry.

The characteristic features of the process which is the object of this invention reside in the succession of operations which will now be described.

1). COLOURING OF THE PURPLE IMAGE.

The side of the film bearing the black and white image corresponding to the mono-chromatic purple image to be obtained is imbibed with water, care being taken so as not to imbibe also the other side of the film.

Among the different known methods adapted for this operation, one of the most practical is the use of a conveniently striated rubber roller part of which is immersed in a container filled with water, the surface of the film which is to be imbibed with water being in contact

with the part of the periphery of the roller which emerges from the water.

The film, one side of which has thus been moistened with water, then passes in a container of convenient shape which is filled with chlorine gas. By contact with the chlorine, the moist silver image is transformed into silver chloride, while the image on the other side of the film, which has remained dry, is not affected by the chlorine.

The whole film is then washed by running water and passed in a solution of sodium sulphite at 1% concentration in order to remove the chlorine which has been absorbed by the gelatine.

After another washing, which removes the sodium sulphite, the film is passed in front of a mercury-vapour lamp to the rays of which the surface bearing the silver chloride image is exposed.

This image is then developed by immersing the whole film in a bath containing thioindoxyl which is alkalised by a small addition of caustic soda and protected against oxidation by a small quantity of sodium sulphite, this bath containing, for example, 10 grams of thioindoxyl, 15 grams of caustic soda, 10 grams of anhydrous sodium sulphate, and water to make 1000 cubic centimetres of solution.

In this manner there is obtained an image wherein the silver chloride has been reduced to metallic silver and at the same time there has been formed a purple image constituted by insoluble thioindigo red.

The film is then rinsed by a jet of water and is dried in the usual manner.

2). Colouring of the Blue-Green Image.

The dry film bearing on one side the red thioindigo image and on the other side the black and white silver image corresponding to the blue-green monochromatic image to be obtained is again imbibed with water by means of a wetting roller, as indicated above in operation No. 1, the said roller now wetting only the silver image intended to form the blue-green image, and not the sound band.

To this effect, the rim of the wetting roller has a width exactly equal to that of the image and the film making contact with the roller is conveniently guided so that the sound band does not touch the water and remains perfectly dry, as well as the thioindigo red image on the other side of the film.

This result being achieved, the whole film is treated as in operation No. 1 by chlorine gas which again affects only the wet part of the film, transforming the silver image carried thereby into silver chloride.

After washing with water and treating with a solution of sodium sulphite at 1% concentration, the silver chloride is exposed to light and then developed by immersing the whole film in a bath containing indoxyl slightly alkalised by caustic soda and protected by a small quantity of sodium sulphite, this bath containing, for example, 10 grams of indoxyl, 15 grams of caustic soda, 10 grams of sodium sulphate, and water to make 1000 cubic centimetres of solution.

In this operation is formed reduced silver and at the same time insoluble indigo blue which forms the blue-green image.

During these treatments, the sound band has undergone no modifications and is always constituted by metallic silver.

According to an advantageous embodiment of the process of this invention, the indoxyl is replaced by 4-chloro-indoxyl which produces, by development of the silver chloride image, a monochromatic blue-green image constituted by dichlorindigo 4 4' the colour of which is much better adapted to the desired trichromatic synthesis than indigo blue.

Furthermore, this chlorine derivative is less subject to oxidation by the air than the indoxyl itself and is better adapted for the composition of the developing bath which is better conserved and more easily used industrially.

The blue-green image being obtained, the film is washed with running water, as in the preceding operations.

These operations have thus resulted in the formation on one side of the film of a purple image mixed with metallic silver, and on the other side of the film of a blue-green image mixed with metallic silver, while the image on the sound band is constituted only by silver.

3). Removal of the Metallic Silver from the Coloured Images.

In order to remove the silver which accompanies the two monochromatic purple and blue-green images without destroying the silver which constitutes the sound band, use is again made of a roller, now partially immersed in a container filled with a bath containing a reagent usually employed in photography for the removal of silver.

This reagent may be, for example: a solution of potassium permanganate or bichromate containing an addition of sulphuric acid, the Farmer mixture (potassium ferricyanide and sodium hyposulphite), or a solution of ammonium persulphate.

Among these reagents for removing the

silver, it is preferred to use the solution of potassium permanganate added with sulphuric acid, its action being followed by a washing with water and by the usual treatment with sodium bisulphite. This process is well adapted to the use of the above described wetting rollers for impregnating the surfaces of the film to be treated, its action is quick and exactly localized, no liquid being applied beyond the surface to be treated.

The indigoid dyes used for the formation of the coloured images being very stable, their colour is not affected by the treatment with the permanganate.

For the removal of the silver accompanying the thioindigo red image, use is made of a roller the rim of which is as wide as the whole film, while for the removal of the silver accompanying the blue-green image the rim of the roller has a width corresponding exactly to that of the blue-green image, so that the sound band or track does not make contact with the said rim. This technique is substantially the same as that which has been used in an earlier operation of this process for wetting the image before chlorinating the same.

It is also evident that the sound band can be placed on the side of the purple image instead of being on the side of the blue-green image, as hereinbefore described, without departing from the scope of this invention. The placing of the sound band on the side of the film which bears the blue-green image has been chosen in view of a modification of the process according to this invention in which this disposition allows the achievement of a result which is advantageous for the sound reproduction.

According to this modification, in the wetting of the side of the film bearing the image to be coloured blue-green, use is made of a wetting roller having the total width of the film band, so that the subsequent chlorination extends not only over the image, but also over the sound band, whereafter the whole is developed into blue-green and the metallic silver is removed only from this image by means of a roller not wider than the said image and imbibing the same with the chosen removing reagent (such as potassium permanganate and sulphuric acid), while the metallic silver it not removed from the sound band.

In this case, the sound band is thus constituted by a reduced silver image mixed with a blue-green dye. It has been found that such a sound band image has a spectral absorption which is adapted for a correct reading of the sound track on a projecting apparatus of the commercial type using photoelectric cells without loss of volume in the sound reproduction, due to the presence of metallic silver in the structure of the sound track, and to the absorption characteristic of the blue-green indigoid dye which has been usd.

However, when it is desired to effect the sensitometer control under the conditions which are usually prescribed for sound recordings on films, it seems to be preferable to operate according to the method as previously described.

4). Obtaining of the Yellow Image.

In order to realise the subtractive trichromatic synthesis, it is now necessary to superimpose in register, to the above described purple and blue-green images, a third, yellow, monochromatic image.

The yellow image is obtained by impregnating the gelatine carrying the purple or the blue-green image with a solution containing a mixture of an alkali diazo sulfonate and a suitable coupling agent. This impregnation may be effected by means of a roller, as aforesaid.

The film thus impregnated is dried and then exposed to the radiation of a powerful mercury-vapour lamp, through the negative film carrying the image selected for violet, and the yellow image completing the trichromatic combination is thus directly obtained.

The film is then washed with water so as to remove the excess of reagents remaining in the gelatine.

As alkali diazo sulfonates giving an insoluble image of the required colour, use is preferably made of those obtained from orthosubstituted amines; it is known that these derivatives possess a higher sensitiveness to light and that they yield dyes the colour of which is more greenish and therefore closer to the ideal primary yellow.

The coupling agents are chosen from the substances giving with diazo amines a yellow dye, preferably aryl derivatives of acetyl-acetic ester, pyrazolones, indols and generally all substances of low moleculur weight having a methylene group which is able to couple.

The following example is given for the solution with which the film is impregnated with a view to the formation of the yellow image: a mixture of ortho chloraniline diazo sulphonate and 1 phenyl 3 methyl 5 pyrazolone alkalised by a small quantity of caustic soda is prepared as follows: 12 grams of ortho chloraniline diazo sulphonate of sodium are dissolved in water to form 500 cubic centimetres of a solution A; 9.5 grams of 1 phenyl 3 methyl 5 pyrazolone are mixed with 20 cubic centimetres of ethyl alcohol or a

glycol derivative to form a paste which is mixed with a solution of 2.5 grams of caustic soda in 50 cubic centimetres of water, and when the paste is dissolved, water is added to form 500 cubic centimetres of a solution B which is filtered; finally, the solutions A and B are mixed in equal quantities.

As the rapidity with which copies of the yellow image are obtained by this diazo sulphonate process is much less than that attained with silver bromide in gelatine, this difference can easily be compensated by using, for obtaining the copies in series, a copying machine having several windows and giving in each operation as many copies exposed through the film carrying the negative record selected for the violet as there are windows provided in the machine.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for producing colour films by subtractive synthesis, comprising producing on the opposite sides of a double-sided film positive silver images by exposing through negatives selected for the green and orange respectively, developing and fixing treating said silver images with chlorine and then with thioindoxyl and indoxyl respectively so as to produce respectively positive purple and blue-green indigoid dye images together with silver images, whereafter the silver image is removed and a positive image of the yellow colour is superimposed on one of said indigoid images by sensitising with a mixture of an alkali diazo sulphonate with a coupling agent such as 1 phenyl 3 methyl 5 pyrazolone which gives the yellow image by exposure to light through the negative selected for the violet.

2. A process for producing colour films as claimed in claim 1, characterized by the fact that it comprises wetting the silver image of the purple monochrome, treating the film with chlorine, so as to transform the silver into silver chloride, removing the chlorine absorbed by the gelatine, exposing the film to light, developing the film in a bath containing thioindoxyl which is alkalised and protected against oxidation, so as to reduce the silver chloride into metallic silver and to form an image of insoluble thioindigo red, wetting the silver image of the blue-green monochrome, treating the film with chlorine, so as to transform the silver into silver chloride, removing the chlorine absorbed by the gelatine, exposing the film to light, developing the film in a bath containing indoxyl which is alkalised and protected against oxidation, so as to reduce the silver chloride into metallic silver and to form an image of insoluble indigo blue, removing the metallic silver from the coloured images by a suitable reagent, sensitising one side of the film with a solution of ortho chloraniline diazo sulphonate and 1 phenyl 3 methyl 5 pyrazolone, and exposing the film to the radiation of a mercury-vapour lamp through the third selected negative, so as to obtain directly the yellow image.

3. A process as claimed in claim 2, wherein the indoxyl used for colouring the blue-green image is replaced by 4-chloro-indoxyl.

4. A process for producing sound and colour films according to any of the preceding claims wherein, after simultaneous impression of the positive images to be coloured purple and blue-green, one on each side of the film, the sound band is impressed on one side of the film, preferably on the side bearing the image to be coloured blue-green, the wetting of said image preparatory to the treatment with chlorine as well as the action of the reagent for removing the silver being limited to said image and excluding said sound band.

5. A process for producing sound and colour films according to any of claims 1 to 3 wherein a sound band is printed on the side of the film bearing the positive silver image to be coloured blue-green and is wetted, treated with chlorine, exposed and developed together with said image, whereafter the metallic silver is removed only from said image.

Dated this 10th day of May, 1946.

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